

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- ① BLACK BORDERS
- ② TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

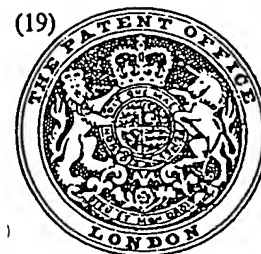
# PATENT SPECIFICATION

(11)

1 448 533

1 448 533

- (21) Application No. 35611/74 (22) Filed 13 Aug. 1974  
 (31) Convention Application No. 91 664/73 (32) Filed 17 Aug. 1973 in  
 (33) Japan (JA)  
 (44) Complete Specification published 8 Sept. 1976  
 (51) INT. CL.<sup>2</sup> C08J 5/22  
 (52) Index at acceptance  
 C3P 7D1C 7D2A1 7D2A2B 7K7 E2 PC13A PC13B PC13C  
 PC17 PC20D2 T1X T2D  
 B5A 1G10 1U2AX 2A3 2D1X  
 C3B 1C12 1C24 1C33A 1C8P 1D2C 1L4E 1L6D



## (54) A PROCESS FOR THE PRODUCTION OF AN ION EXCHANGE MEMBRANE

(71) We, MITSUBISHI PETROCHEMICAL COMPANY LIMITED, a Japanese Body Corporate, of 5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the production of an ion exchange membrane, generally referred to herein as a "heterogeneous membrane", in which a finely divided ion exchange resin is dispersed in a thermoplastic resin matrix.

15 In general, press forming, calender forming and extrusion forming are used as methods of forming sheets and films and, in particular, the method of extrusion forming is favoured when compared to the other forming methods. The methods of press forming and calender forming can be carried out without trouble on a small scale or laboratory scale, but, in the case of the mass production of large size sheets, it is difficult to control the thickness of the sheet accurately; thus requiring expensive apparatus as well as a high degree of skill. Sheets of even thickness can, by contrast, be easily produced on a large scale or a commercial scale by the method of extrusion forming.

20 However, it has hitherto been considered impossible to apply the extrusion forming method of the prior art to the production of an ion exchange membrane. The ion exchange resin is so hygroscopic that the water content can amount to from 4 to 20% when allowed to stand in the air, and, therefore, it produces a large amount of gas during extrusion inside an extruder. Even if an extruder of the "bent type" is used, extrusion can not be practically carried out because of the large amount of gas produced. Furthermore, an ion exchange resin, being crosslinked, is difficult to melt in an ex-

truder, so that many difficulties arise. These difficulties are the lowering of extrusion capacity, the increase of the back pressure and increased fluctuation of the extrusion quantity due to low flow property of the resin; in a manner analogous to the extrusion forming of a resin composition having a high filler content. In order to enhance the electrical conductivity of the resin, which is an important electrochemical property for an ion exchange membrane, it is desirable to increase the quantity of an ion exchange resin being blended; but the increase of the quantity of the ion exchange resin results inevitably in difficulties due to the increasing of the hygroscopic property and lowering of the flow property, as described above.

Efforts have been made to overcome these difficulties and consequently a way has been found to produce an ion exchange membrane on a commercial scale by extrusion. The present invention is based on this discovery.

The above mentioned difficulties can be overcome by a process for the production of an ion exchange membrane consisting of an ion exchange resin finely and heterogeneously dispersed in a thermoplastic resin.

Accordingly the present invention provides a process for the production of an ion exchange membrane comprising a finely divided ion exchange resin heterogeneously dispersed in a thermoplastic resin, which process comprises mixing a thermoplastic resin with substantially dry ion exchange resin powder in the proportions of from 2 : 8 to 8 : 2 parts by weight respectively, preparing pellets from the mixture, adding a lubricant to the mixture, before or after the pelletizing, selected from a metallic soap, a fatty acid amide or a fatty acid ester in a proportion of from 0.1 to 10 parts by weight per 100 parts, by weight of the sum of the weights of the thermoplastic resin and the ion exchange

resin; and then subjecting the pellets to extrusion and to pressing using at least one set of rolls maintained at a temperature of from 50 to 150°C to form the membrane.

- 5 In accordance with the process of the present invention, the extrusion forming or moulding can be carried out on a commercial scale, since the ion exchange resin is pelletized and sealed in a thermoplastic resin, resulting in a marked decrease of the hygroscopic property of the resin. In addition, a lubricant is used which is capable of improving the lubricating property at the boundary of the resin, thus improving the flow property of the resin as well as increasing the efficiency of the extrusion process.

The process of the present invention will now be described in more detail.

- 20 The basic starting materials of the process according to the present invention are an ion exchange resin, a thermoplastic resin, a lubricant and, if necessary, an additive such as a stabilizer.

- 25 The ion exchange resin used may be a cation exchange resin suitable for the production of cation exchange membranes, an anion exchange resin for the production of anion exchange membranes, or a mixture of a cation exchange resin and an anion exchange resin or amphoteric ion exchange resin, for the production of the ion exchange membranes for special uses. The cation exchange resins used may be formed from

- 30 synthetic resins whose base polymers consist of polystyrene, poly (styrene/butadiene), polyvinyl chloride or a phenol-aldehyde resin, and whose ion exchange groups are sulfonic acid, phosphonic acid, phosphinic acid or carboxylic acid groups. The anionic

- 40 exchange resins used may be formed from synthetic resins whose base polymers consist of an epoxy resin, polyvinyl chloride, polystyrene, or a phenol-aldehyde resin and

- 45 whose exchange groups are primary to quaternary amino groups. Above all, it is desirable to use an ion exchange resin having a degree of swelling of 0.5 or more, preferably 3.0 or more, and the resin should

- 50 be stable at the melting point of a thermoplastic resin. By the term "degree of swelling" as used herein is meant the ratio of the volume of the resin in a swollen state to that in a shrunken state during use thereof, as used commonly in the field of ion exchange resins. The ion exchange resin used should have a sufficiently fine particle size and should preferably be a powder of a particle size small than 100 Tyler mesh.

- 60 The choice of the thermoplastic resin used is not particularly critical. Any thermoplastic resin which is comprised of polyethylene, polypropylene, an ethylene-vinyl acetate copolymer; polyvinyl chloride, poly-  
65 styrene or a polyamide may be used, but in

particular, the use of crystalline polyolefins and olefin copolymers such as low density polyethylene, high density polyethylene, polypropylene and the ethylene-propylene copolymers is desirable.

The above mentioned thermoplastic resin and ion exchange fine powder are mixed in a proportion of from 2 : 8 to 8 : 2, preferably from 3 : 7 to 6 : 4. If the proportion of the ion exchange resin used is less than that given in this range, then the ion exchanging property of the membrane cannot be obtained; while if greater, the formation of a coherent membrane will be found to be impossible.

In a preferred embodiment of this invention, an ion exchange resin, a thermoplastic resin and the required additives are mixed or blended while exhausting the generated gas by means of an ordinary melting and blending apparatus such as a kneader or a mixing roll. The blend is then formed in a sheet using rolls and then cut to prepare a pellet-shaped raw material suitable for extrusion. The resulting pellets can be handled as a raw material for ordinary extrusion moulding, since the water content thereof is in general reduced to about 2% and the rate at which moisture is absorbed is much lower than in the case of an ion exchange resin alone. This mixing step is generally carried out using the following operations:

- (a) effective drying of a fine powder of ion exchange resin,
- (b) dispersion of the fine resin powder,
- (c) sealing of the fine resin powder in a thermoplastic resin, thus rendering the ion exchange resin less hygroscopic.

In general, ion exchange resins have a very poor resistance to heat, but, during the mixing and extrusion moulding steps of the present invention, little deterioration takes place upon heating at a temperature of up to 240°C for up to 45 minutes.

It has also been found that the addition of a particular lubricant is markedly effective for improving the flow property and workability of such a resin. The effects are as follows:

- (a) an increase of the rate of extrusion,
- (b) a decrease of the fluctuation of the resultant membrane thickness due to changes in the quantity extruded,
- (c) a suppression of the crack formation that often occurs during thin membrane moulding.

This lubricant is either a metallic soap, a fatty acid amide or a fatty acid ester. The metallic soap used may be a metal salt of a fatty acid having from 10 to 22 carbon atoms, such for example as the calcium, vanadium, cadmium or magnesium salt of stearic acid, palmitic acid or oleic acid. The

polyolefins  
with density  
ethylene,  
propylene

70

ion exchange resin  
mixed in  
: 2, pre-  
the propor-  
ed is less  
n the ion  
rane can-  
he forma-  
be found

75

this inven-  
tion plastic  
are mixed  
generated  
sitting and  
ader or a  
med in a  
o prepare  
itable for  
can be  
inary ex-  
r content  
about 2%  
absorbed  
of an ion  
ig step is  
following

80

powder of

100

in water,  
rendering  
less hygro-

105

is have a  
during the  
eps of the  
tion takes  
ure of up

110

the addition  
y effective  
and work-  
cts are as

115

extrusion,  
on of the  
ess due to  
truded,  
formation  
hin mem-

120

allic soap,  
ester. The  
tal salt of  
22 carbon  
: calcium,  
m salt of  
acid. The

125

fatty acid amide used may be a compound represented by the general formula  $R-CO-NH_2$  in which R represents a saturated or unsaturated hydrocarbon group having from 1 to 21 carbon atoms, or a bis-fatty acid amide represented by the general formula:  $R_1-CO-NH-R_2-NH-CO-R_3$  in which  $R_1$  and  $R_3$  each individually represent a saturated and unsaturated hydrocarbon group having from 9 to 21 carbon atoms and  $R_2$  represents a saturated hydrocarbon group having from 1 to 5 carbon atoms. The fatty acid ester used may be a compound represented by the general formula:

15  $R_1(OH)_n-OOC-R_2$  in which  $R_1$  represents a straight chain or cyclic saturated or unsaturated hydrocarbon group having from 1 to 22 carbon atoms and  $R_2$  represents a saturated or unsaturated hydrocarbon group having from 9 to 21 carbon atoms, and n represents 0 or an integer of 1 or more. Examples of these compounds are oleic acid amide, stearic acid ethylene bisamide, stearic acid monoglyceride, behenic acid monoglyceride, ricinoleic acid monoglyceride, oleic acid monoglyceride, lauric acid sorbitan ester, palmitic acid sorbitan ester and oleic acid sorbitan ester. Sorbitan esters of saturated or unsaturated fatty acids are particularly preferable.

30 It is assumed that since each of the lubricants of a metallic soap, a fatty acid amide or a fatty acid ester type has an alkyl attracting portion and polar attracting portion, an ion exchange resin having a strong polarity can uniformly be dispersed in a thermoplastic resin and, simultaneously, the lubricating property at the boundary of the resin can be improved to increase the flow property of the resin. The electrochemical property of an ion exchange membrane is not lowered even by the addition of such a lubricant.

45 The lubricant is added in a proportion of from 0.1 to 10 parts by weight, preferably from 2.0 to 4.0 parts by weight per 100 parts by weight of the sum of the weights of the ion exchange resin and thermoplastic resin. If the lubricant is added in a proportion of less than 0.1 part by weight, no effect is observed by the addition thereof and a uniform membrane is difficult to mould by extrusion; while if more than 10 parts by weight, the lubricating effect is not significantly increased further and, in addition, the electrochemical exchange property of the resin is sometimes lowered. The addition of the lubricant is ordinarily carried out by adding it to the raw material before the mixing step or by adding it to the mixture before or after the pelletizing step. In view of the ease of operation, the former addition method is preferred.

65 The thus prepared pellets are fed to an

extruder equipped with an ordinary T die to form a membrane which is then subjected to a pressing treatment using rolls such as calendering rolls, followed by rolling-up of the finished membrane. This pressing treatment is carried out for the purpose of cooling and solidifying the membrane and preventing the membrane from shedding some of the ion exchange resin particles during cooling and solidifying and from thus forming pinholes; as well as for giving the surface a smooth and lustrous appearance. The surface temperature of the roll should be kept within a range of from 50 to 150°C, since at below 50°C, the surface of the membrane roughens markedly and, in an extreme case, cracks or pinholes are formed; while at above 150°C, the cooling of the membrane is insufficient, thus resulting in adhesion of the membrane to the roll surface and hence deformation of the membrane. A temperature of from 70 to 130°C is particularly preferably. The pressing treatment is preferably carried out in a multistage process using from two to five pairs of rolls.

The resultant membrane is slightly foamed, but it can be used as an ion exchange membrane as it is. In order to obtain better performance of the ion exchange membrane, the membranes may be subjected to an after-treatment step comprising immersion of the membrane in either a swelling liquid such as an acidic or alkaline solution containing, for example, from 1 to 20% by weight of hydrochloric acid or caustic soda at a temperature of 60°C or higher, or hot water at a temperature of 80°C or higher for several minutes or more.

The following Examples further illustrate the present invention. The mesh standard referred to in these Examples is the Tyler mesh standard.

#### Comparative Example 1

90 parts by weight of styrene monomer and 10 parts by weight of divinylbenzene monomer were copolymerized to give a bridged polystyrene in the form of beads about 1 mm in diameter. These were then sulfonated in a known manner to obtain a cation exchange resin, and then pulverized. The portion of the cation exchange resin passing through a sieve of 100 mesh was used as a raw material, which had a water content of 15% by weight. To 60 parts by weight (on dry base) of this ion exchange resin were added 3 parts by weight of powdered sorbitan stearate as a lubricant followed by mixing for about 10 minutes in a mixer of the high speed revolving blade type. Then 40 parts by weight of powdered polypropylene having a melt index of 5 g/10 min at 230°C was added

thereto and mixed for 10 minutes. The mixed raw material was subjected to extrusion moulding using an ordinary extruder but this extrusion could not be carried out without danger because of small explosions occurring in the cylinder. Thus the extrusion was accomplished using an extruder of bent type (40  $\phi$ , L/D = 27) equipped with an ordinary T die. The optimum conditions were found and used. These were a temperature range of from 155 to 165°C under the hopper, from 180 to 205°C at the bent portion, from 200 to 230°C at the second compression portion and metering portion and from 200 to 230°C at the die portion. Even under the best condition, the quantity of extrusion reached only 6 kg/hr with a screw revolving at 60 rpm and the fluctuation of the rate of extrusion was so large ( $\pm 15\%$  width) that an even, continuing membrane could not be obtained. Furthermore, a vigorous venting of the resin powder took place from the vent hole at the same time.

#### Example 1

In a manner analogous to Comparative Example 1, 60 parts by weight of the ion exchange resin passing through 100 mesh, 3 parts by weight of sorbitan stearate and 40 parts by weight of powdered polypropylene were mixed, kneaded at 185°C for about 30 minutes by means of an ordinary mixing roll and then formed into pellets by the sheet cutting method. The resulting pellets were fed to an extruder provided with an ordinary T die (45  $\phi$ , L/D = 25), extruded in the form of a membrane and pressed by passing through three stage rolls heated to 120°C to obtain in a stable manner a uniform product 0.25 mm in thickness. The rate of extrusion was 11 kg/hr with a screw revolving at 60 rpm and the fluctuation thereof was only up to  $\pm 2\%$ .

#### Example 2

In a manner analogous to Example 1, 60 parts by weight of the ion exchange resin passing through 100 mesh, 3 parts by weight of ethylene-N,N'-methylene-bis-stearamide as a lubricant and 40 parts by weight of powdered polypropylene were mixed and formed into pellets, and then extruded by means of the same apparatus as that of Example 1 thus obtaining a uniform product 0.35 mm in thickness in a stable manner. The rate of extrusion reached 9.8 kg/hr with a screw revolving at 60 rpm and with a fluctuation of up to  $\pm 2\%$ .

#### Comparative Example 2

For comparison with Examples 1 and 2, pellets prepared from 60 parts by weight of the ion exchange resin and 40 parts by weight of polypropylene without adding a lubricant were moulded by the same appa-

ratus as that of Example 1 or 2. However, the fluctuation of the rate of extrusion reached  $\pm 10\%$  or more and cracks were produced from a lower strength area which had been just extruded from the die lips and had not cooled and solidified sufficiently. Thus no product was given. The rate of extrusion was 9.1 kg/hr. When the die temperature was raised to 150°C, some improvement was found with regard to the formation of cracks but the problem could not be solved fundamentally.

#### Comparative Example 3

A membrane was obtained by extruding the same raw material in the same manner as in Example 1 and then the membrane was passed through a three stage roll of iron plated with hard chromium to obtain a product of 0.41 mm in thickness. The surface of the membrane lacked smoothness and lustre and had irregular waved patterns and pinholes on very uneven areas.

#### Example 3

When the membrane-shaped product of Example 1 was treated with hot water for 1 hour and then washed with water, the transport number of the membrane was 0.95 in a 0.5 N NaCl solution and the specific resistance was 180  $\Omega$ cm.

#### Example 4

A fine powder of an anion exchange resin consisting of an epoxy resin as base polymer having amino groups as the exchange groups and passing through 100 mesh was prepared in a known manner. 60 parts by weight of the anion exchange resin, 3 parts by weight of sorbitan stearate as a lubricant and 40 parts by weight of powdered polypropylene were mixed and moulded in a manner analogous to Example 1; thus obtaining a uniform product 0.25 mm in thickness in a stable manner. The rate of extrusion was 12.3 kg/hr with a screw revolving at 60 rpm and with an extrusion fluctuation of  $\pm 3\%$ . The resulting membrane had a transport number of 0.93 in a 0.5 N NaCl solution and a specific resistance of 93  $\Omega$ cm after being treated with hot water for 1 hour and washed with water.

#### WHAT WE CLAIM IS:—

1. A process for the production of an ion exchange membrane comprising a finely divided ion exchange resin heterogeneously dispersed in a thermoplastic resin, which process comprises mixing a thermoplastic resin with substantially dry ion exchange resin powder in the proportions of from 2:8 to 8:2 parts by weight respectively, preparing pellets from the mixture, adding a lubricant to the mixture before or after the pelletizing, selected from a metallic soap, a fatty acid amide or a fatty acid ester in a proportion of from

however,  
trusion  
s were  
ie 70  
suffi-  
1. The  
en the  
, some  
to the 75  
could

truding  
anner 80  
nbrane  
roll of  
obtain  
s. The  
mooth- 85  
waved  
areas.

luct of  
ter for 90  
er, the  
ie was  
nd the

95  
ge resin  
e poly-  
change  
st was  
a by 100  
3 parts  
bricant  
d poly-  
d in a  
; thus 105  
mm in  
rate of  
screw  
trusion  
mem- 110  
0.93 in  
specific  
treated  
ed with

115  
of an  
sing a  
resin  
thermo- 120  
es mix-  
1 sub-  
powder  
8 to  
y. pre- 125  
add-  
re be-  
selected  
nide or  
om 130

5

0.1 to 10 parts by weight per 100 parts by weight of the sum of the weights of the thermoplastic resin and the ion exchange resin; and then subjecting the pellets to extrusion and to pressing using at least one set of rolls maintained at a temperature of from 50 to 150°C to form the membrane.

2. A process as claimed in claim 1 wherein the thermoplastic resin and the ion exchange resin are mixed in the proportion of from 3:7 to 6:4 parts by weight respectively.

3. A process as claimed in claim 1 or claim 2 wherein the lubricant is added to the resin mixture in the proportion of from 2.0 to 4.0 parts by weight of lubricant to 100 parts by weight of the sum of the weights of the thermoplastic resin and the ion exchange resin.

4. A process as claimed in any one of claims 1 to 3 wherein the pressing step is carried out using from two to five pairs of rolls heated to a temperature of from 70 to 130°C.

5. A process as claimed in any one of the preceding claims wherein the lubricant is a sorbitan ester of a saturated or unsaturated fatty acid.

6. A process as claimed in any one of the preceding claims wherein the thermoplastic resin is a crystalline olefin polymer or olefin copolymer.

7. A process as claimed in any one of the preceding claims wherein a stabilizer is additionally present in the resin mixture.

8. A process as claimed in any one of the preceding claims wherein the ion exchange resin has a degree of swelling of greater than or equal to 0.5.

9. A process as claimed in claim 8 wherein the ion exchange resin has a degree of swelling of greater than or equal to 3.0.

10. A process as claimed in any one of the preceding claims wherein the ion exchange resin has a particle size of less than 100 Tyler mesh.

11. A process as claimed in any one of the preceding claims wherein the pressing step is followed by an after-treatment step which comprises the immersion of the membrane in a swelling liquid.

12. A process as claimed in claim 11 wherein the swelling liquid is an acidic solution having a temperature of 60°C or higher.

13. A process as claimed in claim 12 wherein the acidic solution is an aqueous solution containing from 1 to 20 percent by weight of hydrochloric acid.

14. A process as claimed in claim 11 wherein the swelling liquid is an alkaline solution having a temperature of 60°C or higher.

15. A process as claimed in claim 14 wherein the alkaline solution is an aqueous solution containing from 1 to 20 per cent by weight of sodium hydroxide.

16. A process as claimed in claim 11 wherein the swelling liquid is water having a temperature of 80°C or higher.

17. A process as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

18. An ion exchange membrane when produced by a process as claimed in any one of the preceding claims.

MITSUBISHI PETROCHEMICAL  
COMPANY LIMITED,

Per:  
BOULT, WADE & TENNANT,  
34 Cursitor Street,  
London, EC4 1PQ.  
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1976.  
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



